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MOLECULAR SOLVENT-DYNAMICAL EFFECTS ON
ACTIVATED ELECTRON-TRANSFER KINETICS:
HOW IMPORTANT IS SOLVENT FRICTION?

by

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ABSTRACT

The likely extent of retardation exerted by solvent friction upon the rates of activated electron-transfer (ET) processes is explored and evaluated with reference to some extant solvent-dependent data for metallocene ET self exchanges. Barrier-crossing frequencies extracted from the experimental kinetic and barrier data for suitably adiabatic reactions are compared with solvent inertial frequencies (i.e. the zero-friction limit) as estimated from currently available analytic expressions. The additional extent of rate retardation seen in going from low-friction to ostensibly strongly overdamped solvents as deduced in this manner is seen to be substantially muted in comparison with the predictions of conventional Debye-continuum approaches, although follows a solvent functionality that is nevertheless roughly in accord with the latter. The likely importance of more rapid dynamics associated with short-range (molecular) solvation is addressed in the light of these findings.

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INTRODUCTION

Elucidating the various roles of the molecular solvent on the kinetics of activated rate process which occur in such media is a quest that is not only of broadbased fundamental interest and importance, but is seemingly of sufficient nobility to have attained "Holy Grail-like" status in the minds of many experimentalists and some theoreticians. Perhaps inevitably, earlier treatments and discussions focussed on general thermodynamic and activation energetic aspects.¹ Beginning in the late 1970's, and swelling (as in blood clots) during the last decade up to the present time, has been a substantial upsurge of interest in the influence of the solvent upon reaction *dynamics*. Progress has been fueled in particular by extensive developments in the theoretical description of so-called "solvent friction," whereby the net dynamics for activated barrier crossing (and, more generally, along the reaction coordinate) are slowed below the usual values prescribed by transition-state theory (TST) treatments by dissipative energy-transfer effects involving the solvent "bath."² The precise physical meaning and interpretation of solvent-friction effects depend somewhat on the type of chemical process being considered, specifically on the nature of the reaction coordinate. Nonetheless, the usual notion perceives the presence of an impediment to progress along the reaction coordinate as arising from irreversible energy dissipation from the reactive modes to the surrounding solvent. The reaction-coordinate motion is then no longer smooth and unidirectional but is characterized instead by "fits and starts", commonly termed "overdamped motion", perhaps even involving several recrossings back and forth within the barrier-top region before the reaction is finally consummated.²

One important, although historically not the first, class of activated reactions for which the notion of solvent-friction effects has been considered extensively is electron and related charge transfers. (See refs. 3-7 for some

recent overviews). Such systems involve solvent motion as a central component of the reaction coordinate, specifically in the marked changes in the polarization of the solvent dipoles commonly required for the occurrence of charge transfer between reactive sites. This collective dielectric polarization is coupled inherently with charge transfer. However, the rapidity of electronic compared with nuclear motion obliges the latter, including solvent reorganization, to occur at least partly prior to the instant of charge transfer itself, thereby giving rise to the nuclear activation-energy barrier. In cases where solvent reorganization constitutes the predominant contribution to the free-energy barrier, this collective solvent motion necessarily determines the dynamics of approaching, and possibly also surmounting, the activation barrier. As a consequence, one can anticipate that such solvent "dielectric friction" could exert a significant or even substantial influence upon the net barrier-crossing dynamics, and hence on the ET reaction rate.

This intriguing expectation was indeed initiated and then fueled by a number of theoretical contributions appearing in the early/mid 1980's (refs. 8-16 are a very incomplete selection of key papers). The emergence of this theoretical framework spawned a large number of experimental studies aimed variously at probing the nature of, and the extent to which, collective solvent polarization can influence the dynamics of ET and related processes. Broadly speaking, the experimental inquiries fall into four distinguishable (although partly overlapping) categories. The first class (type I) involves the evaluation of time-dependent fluorescence Stokes shifts (TDFS) for solute chromophores forming suitable charge-transfer excited states.^{3,5} In optimal cases, these ultrafast (≥ 50 ps) laser-induced measurements can probe directly the real-time dynamics of polar solvent relaxation around a newly formed solute dipole. The second (type II) concerns a related use of ultrafast pulse lasers to follow

intramolecular ET processes emanating from photoexcited states.⁵ So far, however, almost all of the ET reactions studied in this fashion involve only small free-energy barriers, $\Delta G^* \leq k_B T$ (k_B is Boltzmann's constant).^{5,7}

The remaining two experimental categories constitute attempts to extract information concerning dynamical solvent effects for activated ET processes (say, for $\Delta G^* \geq 5k_B T$). The most common approach (type III) involves the acquisition of solvent-dependent kinetic data for bimolecular outer-sphere electron-exchange reactions, especially symmetrical self-exchange, and for related reactions at electrode surfaces.⁶ The kinetics of the former are most commonly evaluated by means of magnetic resonance (nmr, epr) line-broadening methods. These reaction systems have the obvious virtues of featuring significant (commonly 5-10 $k_B T$) solvent reorganization barriers, thereby being truly activated processes, and provide opportunities to alter systematically the nature of the solute-solvent interactions, reactant electronic structure and vibrational barriers, etc. Indeed, a substantial amount of information regarding solvent dynamical effects can in principle be gleaned from such kinetic data. Despite the clear fundamental importance of activated ET processes, however, the extraction of the required information on barrier-crossing dynamics is often problematical, leading to the publication of a number of rate analyses with accompanying (sometimes wide-ranging) conclusions that the connoisseur (or even casual observer) might justifiably regard as specious at best.

The core of the problem concerns the need to separate the dynamical (preexponential factor) and energetic (barrier height, ΔG^*) contributions to the measured solvent-dependent rate constants. In most cases, the extraction of the desired dynamical information from rate data obliges one to resort to the use of theoretical estimates for ΔG^* , usually having uncertain quantitative validity.

An additional uncertainty in these conventional analyses is that the geometry as well as stability of the precursor complexes for bimolecular (or electrochemical) outer-sphere processes is often unknown.

The conclusions regarding the role of solvent dynamics reached in this fashion are therefore often critically dependent on the validity of the (suspected oversimplified) theoretical models utilized to separate the dynamical and energetic factors. These type III tactics have consequently tended to be regarded as a "poor cousin" in comparison with the more direct (and sophisticated-looking) insight into real-time dynamics obtained from approaches I and II. Nevertheless, in some cases sufficient information on barrier height and related factors can be obtained so to allow more reliable, and even quantitative, deductions to be made regarding the solvent-dependent barrier-crossing dynamics for bimolecular ET reactions (*vide infra*).⁶

Most of the uncertainties faced with such dynamical analyses for activated ET reactions can also be circumvented, at least in principle, by evaluating solvent-dependent rate data for intramolecular (preferably symmetric) ET reactions (labelled here type IV). The evaluation of both the unimolecular ET rates and the barrier heights (the latter from optical ET energies) would provide the preferred route to the separation of dynamical and energetic factors. Unfortunately, however, relatively few type IV systems have been scrutinized usefully so far in the context of solvent dynamics.¹⁷

These overall issues have been reviewed in some detail recently by the present author.^{6a} Broadly speaking, the extant experimental information lends support to the earlier theoretical predictions that overdamped solvent motion ("solvent friction") may influence and even control the ET barrier-crossing dynamics, as prescribed most simply by the longitudinal relaxation time, τ_L , in a number of cases. However, several interesting and even crucial issues remain

largely undiscussed as well as unresolved. One nagging question involves the differences between the dynamics of short-range (molecular-scale) solvation, which should provide a dominant part of the net solvent friction, and the inherently *long-range* solvent dynamics considered in the dielectric-continuum models which are commonly utilized in data analyses. While the latter (described for Debye solvents simply by τ_L^{-1}) correlates with the solvent-dependent barrier-crossing rates in a number of experimental systems,⁶ one has good reason to be suspicious of the common inference that τ_L^{-1} "describes the relevant dynamics." A related problematic issue is the widespread observation (or claims!) of such rate- τ_L^{-1} correlations, especially for electrochemical reactions,^{6a} even though established electron-tunneling treatments predict their occurrence *only* as limiting cases for ET reactions displaying unusually strong donor-acceptor electronic coupling.¹⁸

The purpose of the present paper is to address in straightforward descriptive fashion these questions concerning ET barrier-crossing rates in the light of current notions concerning *molecular* solvent dynamics, that is, concerned especially with short-range solvation. The basic tenet involves the use of selected experimentally derived data for barrier-crossing frequencies in comparison with expectations from theoretical models in order to assess the validity of conventional descriptions of solvent-friction effects in ET reactions.

Extraction of Solvation Dynamical Information for Activated ET Processes

We consider, as before, homogeneous-phase ET reactions having the general form



where Ox and Red refer to oxidized and reduced forms of a given redox couple. We are concerned primarily with self-exchange reactions, where $\text{Ox}_1 = \text{Ox}_2$ and $\text{Red}_2 = \text{Red}_1$, so that the free-energy driving force, ΔG° , is zero, and the reaction is chemically as well as energetically symmetrical. The Ox and Red sites may reside on separate solute species (intermolecular ET), or may be bound chemically to each other (intramolecular ET). Experimental kinetic results for only the former type (III above) will be considered here.

The role of the dynamics of nuclear modes, including those associated with solvent reorganization, upon the rate constant for electron exchange, k_{ex} , is commonly expressed in terms of the nuclear barrier-crossing frequency, ν_n (s^{-1}), by means of the simplified expressions⁶

$$k_{ex} = K_p k_{et} \quad (2a)$$

where

$$k_{et} = \kappa_{el} \nu_n \exp(-\Delta G_i^*/k_B T) \quad (2b)$$

Here ΔG_i^* is the intrinsic free-energy barrier, κ_{el} is the electronic transmission coefficient, and K_p is the preequilibrium constant describing the statistical probability of finding the reactant pair in an internuclear configuration suitable for electron transfer. For intramolecular ET, the desired "unimolecular" rate constant k_{et} (s^{-1}) is usually measured directly, whereas for bimolecular reactions it is necessary to estimate k_{et} from the measured rate constant k_{ex} by means of formal expressions such as Eq. (2a).

A central fundamental issue that has incurred much discussion is the manner and extent to which overdamped solvation dynamics ("solvent friction") may limit the measured rate constant by affecting ν_n .⁶ An important aspect of this question concerns the relative roles of donor-acceptor electronic coupling and nuclear dynamics in determining the overall preexponential factor A_{et} ($= \kappa_{el} \nu_n$).

Simply, for systems where the electronic coupling (as prescribed by the electronic matrix coupling H_{12}) is small (typically, say, $< 0.5 \text{ kJ mol}^{-1}$), A_{et} will be dominated by the electron-tunneling probability within the transition state, and the nuclear dynamics (ν_n) should exert little or no influence upon A_{et} ("nonadiabatic ET"). Only for systems where the electronic coupling is sufficient to yield adiabatic pathways ($\kappa_{e1} \rightarrow 1$) will nuclear dynamics constitute the dominant contribution to A_{et} . The latter situation corresponds to the reaction dynamics being describable in terms of motion along a single hypersurface continuously from equilibrium reactants to products. Most significantly from an experimental perspective, therefore, the crossover from largely nonadiabatic to adiabatic behavior is expected to be signaled by a marked alteration in the solvent-dependent kinetics in that the reaction dynamics should be sensitive to the solvation dynamics only in the latter case.¹⁸

In our laboratory, this prediction turned out to have a major beneficial influence on our efforts to disentangle solvent dynamical effects from the other factors which may influence the rates of type III ET processes. Rate data for a series of metallocenium-metallocene ($\text{Cp}_2\text{M}^{+/0}$, where Cp = cyclopentadienyl and derivatives) self-exchange reaction were obtained in a number of solvents with suitably varied dynamical properties.¹⁹⁻²² [The reasoning behind the choice of these systems as "model probe reactants" for solvent dynamical studies is detailed in the original papers. Nonetheless, worthy of mention here is the availability of experimental estimates of ΔG_1^\ddagger from optical ET energies for mixed-valence $\text{Cp}_2\text{Fe}^{+/0}$ dimers,^{24,25} which facilitate the (hopefully) reliable separation of energetic and dynamical factors (vide supra).] While not evident initially,¹⁹ subsequent work identified clearly a crossover in the solvent-dependent kinetics from the relatively slow reactions (exemplified by $\text{Cp}_2\text{Fe}^{+/0}$), which display virtually *solvent-independent* dynamics, to more facile processes (such as for

$\text{Cp}_2\text{Co}^{+/0}$ derivatives) that yield approximately τ_1^{-1} -dependent dynamics.²⁰⁻²² Moreover, this transitional behavior was found to be consistent with theoretical H_{12} estimates for $\text{Cp}_2\text{M}^{+/0}$.^{22,23}

Besides the intrinsic significance of the observed nonadiabatic-adiabatic crossover, the results provide an unusual (even, we believe, so far unique) opportunity to assess the validity of the kinetic data analysis utilized for extracting solvent-dependent dynamical information. Most simply, one can crosscheck the absolute magnitude as well as the solvent dependence of the A_{st} values obtained from the experimental k_{ex} and ΔG_1^\ddagger values by using Eq. (2) or related, more sophisticated, expressions.²⁰⁻²² As a consequence, we have some confidence (so far!) in at least the semiquantitative validity of estimates of A_{st} and related quantities extracted from $\text{Cp}_2\text{M}^{+/0}$ self-exchange data. We cannot make a similar claim for any other type III system studied to date.

Estimation of Inertial Solvation Dynamics

Given this scenario, it should be instructive to compare further this experimentally derived information on solvent-dependent barrier-crossing dynamics, published now four years ago, with the expectations of current, especially molecular-based, models of solvation dynamics. Of particular significance in this regard is the extent to which overdamped, rather than inertial, solvent motion controls the barrier-crossing dynamics in adiabatic ET processes. The latter situation corresponds to the occurrence of the transition-state theory (TST) limit, where solvent-friction effects are absent. In this case, ν_n will be determined instead by the "free" rotational dynamics of individual solvent dipoles, so that $\nu_n = \omega_0/2\pi$, where ω_0 is this inertially limited frequency.

An interesting means of gauging the importance of solvent-friction effects

is to assess the degree to which the experimental solvent-dependent values of $\kappa_{e1}\nu_n$ for adiabatic ET processes (where $\kappa_{e1} \rightarrow 1$) fall below the anticipated solvent inertial frequencies. To be numerically worthwhile, such a comparison would desire the receipt of relatively reliable estimates of $\omega_0/2\pi$ (say, within twofold). Following earlier treatments,^{9,11} a pair of analytic expressions for ω_0 can be derived.²⁶ The first can be expressed as

$$\omega_0 = \omega_f [(2\epsilon_s + \epsilon_\infty)/3\epsilon_\infty g_k] \quad (3)$$

Here ϵ_s and ϵ_∞ are the static and "infinite-frequency" dielectric constants, g_k is the Kirkwood g-factor, and ω_f is the "free rotor" frequency given by $(2k_B T/I)^{1/2}$, where I is the solvent molecular moment of inertia (as extracted from gas-phase microwave spectra). The square-bracketed term in Eq. (3) describes how the effective solvent rotational frequency is accelerated by the presence of the surrounding dielectric medium (vide infra).

The second expression for ω_0 can be obtained from Eq. (72) of ref. 9, which can be written as²⁶

$$\omega_0 = \omega_f [3y\epsilon_s/(\epsilon_s - 1)]^{1/2} \quad (4)$$

The reduced concentration of solvent dipoles, y , is given by

$$y = 4\pi\rho\mu^2/9k_B T \quad (4a)$$

where ρ is the solvent number density and μ is the dipole moment. The close relationship between Eq. (4) and the alternative expression for ω_0 , Eq. (3), is exposed by writing the Kirkwood g-factor, appearing in the former relation, as²⁷

$$g_k = \frac{9k_B T}{4\pi\rho^2} \frac{(\epsilon_s - \epsilon_\infty)(2\epsilon_s + \epsilon_\infty)}{\epsilon_s(\epsilon_\infty + 2)^2} \quad (5)$$

Equations (3) and (4) are equivalent when g_k is given by Eq. (5), in the limit

where $\epsilon_\infty = 1$. This circumstance is tantamount to neglecting the electronic polarization of the solvent medium.

An illuminating discussion of the factors influencing solvent inertial dynamics, utilizing essentially Eq. (4), has been presented recently by Maroncelli et al.²⁸ They employed (and derived) Eq. (4) expressed in the form

$$\omega_0^2 = \alpha \omega_I^2 \quad (6)$$

where the coefficient α is given by

$$\alpha = (4\pi\rho\mu^2/3k_B T)(1 - \epsilon_s^{-1})^{-1} \quad (6a)$$

Given that $\epsilon_s \gg 1$ for polar solvents, so that $(1 - \epsilon_s^{-1}) \approx 1$, this formulation emphasizes how the effect of the dielectric environment on the inertial dynamics is predicted to be dominated *simply* by the solvent dipole density as gauged from the $\rho\mu^2$ term. Maroncelli et al found support for the validity of Eq. (6a) from the approximate agreement between the ω_0 values predicted in this fashion and those obtained from MD simulations for several solvents, including acetonitrile and water.²⁸ Since the latter calculations refer largely to solvation dynamics involving spherical solutes, they would appear to have direct relevance for predicting the inertial dynamics associated with short-range solvation in addition to the "bulk-phase" solvent to which such dielectric continuum models usually refer. One therefore has a firm basis for confidence in the usefulness of Eq. (4) for estimating inertial solvation dynamics in activated ET processes.

At first glance, a limitation of Eqs. (4) and (6a) would appear to be the neglect of the high (optical) frequency dielectric constant, which is included in the alternative formulation Eq. (3). Combining Eqs. (3), (5) and (6) yields

$$\alpha = (4\pi\rho\mu^2/3k_B T) \left[\frac{\epsilon_s(\epsilon_\infty + 2)^2}{9\epsilon_\infty(\epsilon_s - \epsilon_\infty)} \right] \quad (6b)$$

where the term in square brackets now replaces the $(1 - \epsilon_s^{-1})^{-1}$ term in Eq. (6a). Interestingly, however, the former term is consistently close to unity (within ca 20%) for values of ϵ_s and ϵ_∞ (≥ 20 and 2-4, respectively) typical for polar solvents, so that the inclusion of the electronic polarizability of the solvent molecules (via ϵ_∞) exerts little numerical influence upon the estimation of ω_0 . The central role of the dipole density in prescribing the effect of the surrounding dielectric medium upon the inertial frequency is therefore an intriguing hallmark of both formulations, Eqs. (3) and (4).

Assessment of Rate Retardation by Solvent Friction

On the basis of the foregoing, the comparison between the solvent-dependent barrier-crossing frequencies, $\kappa_{s1}\nu_n$, derived from the $\text{Cp}_2\text{M}^{+/0}$ rate and energy barrier data with inertial frequencies estimated from Eqs. (3) and (4) should provide at least semiquantitative insight into the degree to which overdamped dynamics (solvent friction) may diminish the rate below the adiabatic TST limit. To this end, Table I displays $\kappa_{s1}\nu_n$ values evaluated for three metallocene self-exchange reactions in eleven solvents, listed alongside the corresponding solvent inertial frequencies, $\omega_0/2\pi$, as estimated from Eq. (3). (See refs. 20 and 21 and footnotes to Table I for data and kinetic analysis used to obtain $\kappa_{s1}\nu_n$ values; see footnotes to Table II and Fig. 4 of ref. 29 for ω_0 calculational details.) The three metallocene couples consist of a pair of cobaltocene systems, $\text{Cp}_2'\text{Co}^{+/0}$ and $\text{Cp}_2^*\text{Co}^{+/0}$ (Cp' - pentamethylcyclopentadienyl, Cp^* - carboxymethyl derivative), that follow largely adiabatic pathways, and one example, $\text{Cp}_2\text{Fe}^{+/0}$, that displays the hallmarks of reaction nonadiabaticity.²² The latter behavior is evidenced most clearly from the observed insensitivity of the $\kappa_{s1}\nu_n$ values for the ferrocene couple to the solvent dynamics, as assessed conventionally by the τ_L^{-1} values that are also listed in Table I. In contrast, the cobaltocene reactions

display markedly (ca 10-100 fold) larger barrier-crossing frequencies; moreover, the $\kappa_{01}\nu_n$ values correlate roughly with the anticipated solvent dynamics, at least in the "Debye" (first nine) solvents listed in Table I. This correlation is in approximate concordance with the expectation that solvent dynamics controls the adiabatic barrier-crossing frequency, since according to the simplest overdamped dielectric-continuum models one anticipates that⁶ $\nu_n \sim \tau_L^{-1}$ (but see below). We have discussed at length elsewhere this issue with respect to the metallocene reactions.^{21,22} In particular, a more detailed analysis of the variations in the rate-solvent dependencies for the different metallocene self-exchanges enabled estimates of the electronic coupling to be deduced.²² Thus for the largely adiabatic cobaltocene couples, $H_{12} \sim 0.2$ to 5 kJ mol^{-1} , whereas for the more nonadiabatic ferrocene systems, $H_{12} \sim 0.4 \text{ kJ mol}^{-1}$.

A close comparison of the solvent-dependent cobaltocene $\kappa_{01}\nu_n$ values with the corresponding $\omega_0/2\pi$ as well as τ_L^{-1} values in Table I, however, suggests that a significantly different picture of the role of solvent dynamics may be more appropriate. Specifically, the $\kappa_{01}\nu_n$ values for both cobaltocene reactions lie almost uniformly within ca twofold of the predicted inertial barrier-crossing frequencies, $\omega_0/2\pi$, in each solvent, implying that the actual frictional retarding effect is no more than small or moderate. This observation, of course, must be tempered by the recognition of the likely uncertainties (probably around twofold or so) in estimating $\kappa_{01}\nu_n$ as well as ω_0 . Nevertheless, when fueled by the likely reliability of the inertial frequency estimates as noted above, one seemingly has grounds for doubting the oft-perceived dominance of overdamped, rather than inertial, solvent dynamics in adiabatic ET barrier crossing even for systems such as the metallocenes where solvent reorganization forms the predominant barrier component. Thus taking the $\kappa_{01}\nu_n$ and $\omega_0/2\pi$ estimates at face value, the degree to which solvent friction retards the barrier-crossing

frequency below the inertial (TST) limit would appear to be no more than 2-3 fold, even in supposed "slow well-overdamped" solvents such as benzonitrile, TMU, and HMPA.

It is appropriate, however, to review briefly the basis of our earlier suggestion that overdamped dynamics provide a predominant influence upon ν_n for such ET reactions.^{6,19-22} The $\kappa_{e1}\nu_n$ values obtained for the adiabatic (or near-adiabatic) reactions decrease by 10-20 fold in going from dynamically fast (and low friction) solvents such as acetonitrile and water to "slow overdamped" media such as TMU and HMPA (Table I). While the corresponding variations in the τ_L^{-1} values are somewhat larger, 20-30 fold, such sub-unit $\log \kappa_{e1}\nu_n - \log \tau_L^{-1}$ slopes are expected even on the basis of simple overdamped solvent dynamical models on several grounds.^{6a} Most generally, the estimation of solvent-dependent $\kappa_{e1}\nu_n$ values presuming a fixed precursor stability (K_p), as was done in assembling Table I, is an oversimplification. K_p is actually anticipated to diminish progressively as ν_n increases as a result of systematic alterations in the distribution of encounter geometries contributing to the measured bimolecular rate constant.^{6a,18} (This effect can partly be accounted for within the framework of the "fixed K_p " analysis by noting that κ_{e1} for near-adiabatic reactions should decrease as ν_n increases.¹⁸) A formally more precise analysis involves the comparison of observed rate-solvent dependencies with the corresponding calculated behavior that accounts for precursor geometry and other complicating features: such a procedure applied to the metallocene systems yielded valuable insight into the role of electronic coupling.^{6,22} In addition, the presence of reactant vibrational contributions to the ET barrier can also diminish the $\kappa_{e1}\nu_n - \tau_L^{-1}$ dependence,¹² even though the observed attenuation appears typically to be milder than predicted.³⁰

Several theoretical expressions emanating from the dielectric-continuum

model provide estimates of the extent of solvent frictional retardation of the ET barrier-crossing dynamics for certain specific forms of the free-energy barrier. The first such description of the interplay between overdamped and inertial solvent dynamics was given by Calef and Wolynes.⁹ Their expression for the adiabatic barrier-crossing frequency for electron-exchange processes can be written as³⁴

$$\nu_n = (2\pi c \tau_L)^{-1} [0.5 + 0.5 (1 + \frac{2}{c^2 \epsilon_s \gamma} \cdot \frac{\tau_{rot}^2}{\tau_L^2})^{1/2}]^{-1} \quad (7)$$

Here $\gamma = \{3y/(\epsilon_s - 1)\}$ [Eq. (4a)], $\tau_{rot} = (\omega_f)^{-1}$, and c is a so-called barrier "shape factor."⁹ For cusp-like barriers, i.e. $H_{12} \ll k_B T$, this quantity is given approximately by $c = (k_B T)/\pi \Delta G^*$. In the limit where $\tau_{rot} \ll \tau_L$, Eq. (7) reduces to the well-known expression for overdamped dynamics within a cusp barrier⁸

$$\nu_n = \tau_L^{-1} (\Delta G^*/4\pi k_B T)^{1/2} \quad (8)$$

In the inertial limit, i.e. where $\tau_{rot} \gg \tau_L$, we recover the TST formula

$$\nu_n = \omega_0/2\pi \quad (9)$$

The "shape factor" c in Eq. (7) accounts for the effects of barrier-top roundedness brought about by donor-acceptor electronic coupling. Since c increases towards larger H_{12} , Eq. (7) predicts that the barrier-crossing frequency in the presence of solvent friction will diminish as the barrier top becomes more rounded (i.e. less cusp-like).³⁵ This barrier-shape dependence of the reaction dynamics, which is absent in the TST (inertial) limit, arises physically from the additional "recrossings" associated with overdamped solvent motion that are anticipated as the barrier top becomes broader.

An alternative combined formulation of overdamped and inertial motion,

which emphasizes more explicitly the influence of barrier-top dynamics on the barrier-crossing frequency, has been described by Hynes.¹¹ This treatment pictures the overall adiabatic rate constant, k_A , as a composite of the rate for crossing the barrier top, k_b , and for motion within the parabolic wells, k_w , according to¹¹

$$k_A^{-1} = k_b^{-1} + 0.5 k_w^{-1} \quad (10)$$

While solvent friction is included in the analytic expressions for both k_b and k_w , for reasons of consistency solvent inertia is considered only in the former component.²⁹ Nonetheless, for Debye solvents the Hynes formulation [Eq. (10)] yields comparable numerical results to the Calef-Wolynes expression [Eq. (7)]. A key advantage of the former, however, is that it is designed to be applicable in the presence of so-called "frequency-dependent solvent friction."¹¹ This circumstance includes not only that encountered necessarily in non-Debye solvents²⁹ but also for nonexponential decay dynamics arising from molecular solvation effects.³⁶ Additionally, the Hynes formulation provides a more generally useful treatment of barrier-shape effects upon the barrier-crossing dynamics. Thus for cusp barriers, $k_b \gg k_w$ so that well relaxation dominates; k_b will decrease, however, as the barrier top becomes broader so that eventually $k_b \leq k_w$, whereupon the net rate will diminish to the point where it is controlled by solvent dynamics within the barrier-top region.²⁹

At least in Debye media, both formulations predict that the inertial dynamics exert an important limiting influence on ν_n only in "low-friction" media such as acetonitrile and acetone, the barrier-crossing frequency in higher-friction media such as benzonitrile [where $(\omega_0/2\pi) \geq 2\tau_L^{-1}$] being controlled almost entirely by overdamped solvent dynamics.^{29,34} Given that the near-adiabatic cobaltocene-based reactions in Table I necessarily feature substantial

barrier-top roundedness [$H_{12} = 2-4 \text{ kJ mol}^{-1}$ (vide supra)²²], it is of particular interest to consider the solvent-dependent barrier-crossing frequencies predicted from Eq. (10) under these conditions. Listed in Table I are ν_n values, labelled ν_n^H , calculated from the Hynes formulation, Eq. (10), by means of the dielectric-continuum model using the ω_0 and τ_L values listed alongside, with k_b estimated for $H_{12} = 2.1 \text{ kJ mol}^{-1}$. (This matrix coupling value is appropriate for the cobaltocene reactions considered in Table I.)²² For the non-Debye solvents included in Table I, propylene carbonate (PC) and methanol, the distribution of relaxation times indicated in the dielectric loss spectra is taken into account when estimating k_b and k_u . Further details of the calculational procedures are given in ref. 29. The ν_n^H values listed in Table I are markedly (3-4 fold) smaller than τ_L^{-1} , reflecting the predicted sluggishness of surmounting the barrier with a well-rounded top by means of overdamped solvent motion.

Comparison of these ν_n^H estimates with the experimental $\kappa_{s1}\nu_n$ values for the cobaltocene reactions in Table I shows that the latter are typically 3-10 fold larger. Recalling our observation above that the $\kappa_{s1}\nu_n$ values tend to lie only twofold or so below the corresponding TST limit, $\omega_0/2\pi$, one may conclude that the extent of solvent friction as predicted from the most relevant dielectric-continuum approach is rather more pronounced than occurring experimentally, at least for the metallocene systems. Stated more precisely, the experimental extent of rate retardation by solvent friction, defined as k_{TST}/k , would appear to be only ca 2-3 even in the most overdamped solvents in Table I, rather than the tenfold or so predicted from the dielectric-continuum approach.

Whither Solvent Friction?

Given this deduction, it is of interest to consider likely factors that may account for the apparent breakdown of the usual continuum model of dielectric

friction for activated ET processes. Even within the confines of dielectric-continuum solvent models, there are good reasons to doubt the general quantitative relevance of τ_L^{-1} to ET barrier-crossing dynamics. The commonly anticipated presence of faster dissipative solvent relaxation modes, observed directly in some TDFS experiments,³¹ should accelerate the net overdamped barrier crossing.^{11,32} This behavior, most clearly discerned for the metallocene reactions in methanol and other non-Debye media,^{29,33} may well occur more generally. Furthermore, unlike the solvent inertial motion noted above, the longitudinal overdamped dynamics associated with short-range solvation are anticipated to differ significantly or even markedly from the continuum (zero-wavevector) description that offers τ_L^{-1} as the relevant parameter. This is clearly a central issue since short-range solvation should inevitably provide the major contribution to the solvent dynamics as well as the reorganization energetics.

A number of recent theoretical and simulational studies have endeavored to ascertain the characteristics of such molecular-level solvation dynamics. While limited so far to relatively low-friction media, molecular dynamics simulations have proved to be a particularly insightful approach (refs. 39-47 are representative). A common finding from these studies is the presence of a rapid initial solvation response to the solute charge change, approaching that anticipated for inertial solvent motion²⁸ followed by slower dynamics more characteristic of overdamped relaxation. As pointed out by Carter and Hynes,⁴³ the former feature is missing from conventional analytic theories of solvation dynamics, although recent treatments have endeavored to include it.¹⁶ Since the inertial component can typically constitute a large (> 50%) fraction of the simulated time-correlation function, such rapid molecular dynamics might well be anticipated to provide an important or even dominant contribution to ET barrier-

crossing dynamics. Unfortunately, however, there are at present no theoretical treatments of this issue that yield clearcut numerical predictions. It also remains to be seen if such rapid short-range solvation dynamics will be characteristic also of ostensibly higher-friction media where overdamped motion is conventionally regarded as the dominant factor in the barrier-crossing dynamics.

Some experimental information on the disparities between molecular solvation dynamics and the dielectric-continuum predictions has also been obtained from suitably ultrafast TDFS measurements.⁴⁸ The data indicate the presence of relaxation components that are significantly more rapid as well as slower than anticipated from the dielectric-continuum treatment. The solvents studied include anticipated overdamped media such as dimethylsulfoxide and dimethylformamide.⁴⁸ While limited inevitably by the pulse laser risetime (ca 0.1 ps), these findings suggest the presence of unexpectedly rapid molecular (presumably short-range) solvent relaxation. Similarly to non-Debye continuum circumstances, such faster molecular-based relaxation components are anticipated to dominate the net barrier-crossing frequency for adiabatic activated ET processes.^{11,29,32}

Consequently, then, the observation that $\nu_n \sim \tau_L^{-1}$ for near-adiabatic ET reactions, as exemplified in Table I, may arise from a fortuitous (albeit rough) compensation between the influence of short-range solvation dynamical components that tend to be more rapid than long-range (continuum) solvent relaxation, offset by the relative inefficiency by which round-top barriers can be surmounted in the presence of overdamped motion. This deduction bears a resemblance to the conclusion of a recent MD simulation study of ET barrier-crossing dynamics in a model polar solvent, where the ν_n values were found to fall only marginally (twofold or less) below the TST prediction, and then only for barrier-top

curvatures corresponding to considerable electronic coupling ($H_{12} = 20 \text{ kJ mol}^{-1}$).^{46,49} (The latter finding implicates the importance of frictional retardation in the barrier-top region, rather than in the wells, à la the Grote-Hynes description.⁵⁰) However, the simulated solvent employed in ref. 46 is only marginally overdamped, $\omega_0/\tau_L^{-1} = 2.5$ (i.e. comparable to acetonitrile or acetone in this respect), so that the relevance of the findings to ostensibly higher-friction media is presently unclear.

Nonetheless, in a more general vein the deduction of smaller frictional retardation effects than anticipated from conventional zero-wavevector/Debye treatments is perhaps unsurprising given the anticipated occurrence of frequency-dependent solvent friction in the context of the Grote-Hynes description of activated barrier crossings.^{2b,11} This treatment predicts that the barrier-crossing dynamics can be dominated by higher-frequency (i.e. faster relaxation) components of the molecular solvation, especially when the barrier top is relatively sharp. Consequently, the actual rate retardation in more overdamped solvents may be muted substantially in comparison with that anticipated on the basis of the major, yet often slower-relaxing, components of the overall friction kernel that are commonly considered in Debye-continuum treatments of dielectric friction.

In conclusion, one is left with an uneasy feeling of only partial understanding of the problem being achieved, tempered with substantial uncertainty as to the underlying physical solvation factors responsible for, as well as the numerical importance of, solvent-friction effects in activated ET processes. A major hurdle to the exploration of solvent friction in conventional (i.e. activated) chemical process clearly remains the extraction and diagnosis of dynamical factors in the inevitable presence of the other obfuscating effects that abound in most reaction systems. The above discussion has tried to

emphasize that even for bimolecular processes useful, at least semiquantitative, information on solvent-dependent dynamical factors can be obtained for favorable cases. Further experimental efforts for ET processes, however, would perhaps be most insightfully directed to intramolecular systems. Such data, particularly with information from MD simulations for a wider range of solvating media, may well spawn a new chapter in our molecular-level understanding of solvent-friction effects in activated chemical processes.

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TABLE I Comparison Between Solvent-Dependent Barrier-Crossing Frequencies for Selected Metallocene Self Exchanges and Predicted Inertial and Overdamped Solvent Frequencies

SOLVENT ^a	$\omega_0/2\pi$ ^b s ⁻¹	τ_L^{-1} ^c s ⁻¹	ν_n^B ^d s ⁻¹	$\kappa_{el}\nu_n$ s ⁻¹ ^e		
				Cp ₂ 'Co ⁺⁰ ^f	Cp ₂ [*] Co ⁺⁰ ^g	Cp ₂ Fe ⁺⁰ ^h
Acetonitrile	2×10 ¹²	4×10 ¹²	1.2×10 ¹²	5×10 ¹²	2.5×10 ¹²	3×10 ¹¹
Acetone	1.0×10 ¹²	3.5×10 ¹²	6.5×10 ¹¹	3×10 ¹²	2×10 ¹²	4×10 ¹¹
Water	7×10 ¹²	1.9×10 ¹²	7.5×10 ¹¹		3.5×10 ¹²	
Nitromethane	1.6×10 ¹²	4.5×10 ¹²	8×10 ¹¹		3×10 ¹²	4×10 ¹¹
DMSO	1.5×10 ¹²	5×10 ¹¹	1.7×10 ¹¹	1.0×10 ¹²		1.5×10 ¹¹
Benzonitrile	6.5×10 ¹¹	2×10 ¹¹	5.5×10 ¹⁰	7×10 ¹¹	3×10 ¹¹	2.5×10 ¹¹
Nitrobenzene	~ 6×10 ¹¹	2×10 ¹¹	6.5×10 ¹⁰		1.5×10 ¹¹	2.5×10 ¹¹
TMU	8×10 ¹¹	1.7×10 ¹¹	6×10 ¹⁰		3×10 ¹¹	
HMPA	~ 6×10 ¹¹	1.1×10 ¹¹	4×10 ¹⁰	2.0×10 ¹¹		
PC	1.5×10 ¹²	(4×10 ¹¹)	2×10 ¹¹	2.5×10 ¹²	1.5×10 ¹²	3.5×10 ¹¹
Methanol	1.7×10 ¹²	(1.3×10 ¹¹)	4×10 ¹¹		1.5×10 ¹²	4.5×10 ¹¹

^a DMSO - dimethylsulfoxide, TMU - tetramethylurea, HMPA - hexamethylphosphoramide, PC - propylene carbonate.

^b Predicted adiabatic TST barrier-crossing frequency in given solvent, from Eq. (3). (See footnotes to Table II and Fig. 4 of ref. 29 for calculational details.)

^c Inverse longitudinal relaxation time of pure solvent, as extracted from dielectric loss spectra (from Table I of ref. 22). Values given in parentheses refer to major relaxation for solvents also exhibiting higher-frequency dispersion (non-Debye behavior).

^d Adiabatic barrier-crossing frequency, calculated from Eq. (10) by using dielectric continuum model, assuming $H_{12} = 2.1$ kJ mol⁻¹ (see text and ref. 29 for details).

^e Barrier-crossing frequencies for metallocene redox couple in given solvent, as extracted from rate constants and barrier heights (obtained from nmr line broadening and near-infrared optical measurements, respectively) by using Eqs. (2a) and (2b). See Table I of ref. 22 for experimental data, and ref. 21 for procedural details. Value of precursor stability constant, K_p , taken as 0.25 M⁻¹. Barrier heights for Cp₂'Co⁺⁰ and Cp₂^{*}Co⁺⁰ reactions diminished by 2.1 and 3.1 kJ mol⁻¹, respectively, to allow for electronic coupling (ref. 22).

^f Cp₂'Co⁺⁰ - decamethyl(cobaltocenium - cobaltocene).

^g Cp₂^{*}Co⁺⁰ - carboxymethyl(cobaltocenium - cobaltocene).

^h Cp₂Fe⁺⁰ - ferrocenium - ferrocene.